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THE CONVERSION OF GAS OIL IN A RAPID CRACKING PROCESS USING CRACKING CATALYST AND SILICA SAND HEAT CARRIERS [Part of Energy, Mines and Resources 50/50 Cost-Shared Energy Conversion Program and part of the program of the Federal Panel on Energy R & D (PERD)]

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Final Report
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ABSTRACT

A preliminary investigation of the conversion of gas oil to chemical intermediates (i.e., olefins, petrochemicals) and light transportation fuels (i.e., gasoline) was carried out in Ensyn's Rapid Thermal Processing (RTP) pilot plant. The plant is rated nominally at 1 barrel per day, and is equipped with a novel reactor system to accomplish very fast heat transfer and short residence times over a broad range of reaction temperatures.

During the project, nine experiments were completed. Six of these experiments included a non-catalytic heat carrier (i.e., silica sand) to transfer heat to the reactor system. In the remaining three experiments a catalytic heat carrier (i.e., an aluminosilicate cracking catalyst) was used. Complete mass balance procedures were carried out during all of the experiments in order to verify the estimates of the product yields.

The highest non-optimized gasoline yield was 16.2%, by mass, of the gas oil feedstock. This yield occurred using the catalytic heat carrier at a reaction temperature of 575 °C and a residence time of 500 milliseconds. The maximum (non-optimized) gasoline yield using a non-catalytic heat carrier was 15.1%, and occurred at a reaction temperature of 840 °C and a residence time of 340 ms. The use of catalyst had a dramatic effect on gasoline yields for a given reaction temperature.

The highest (non-optimized) yield of the fraction boiling in the decant range was 25.8%, by mass, of the gas oil feedstock, using a catalyst heat carrier at 670 °C and 390 ms.

The highest olefin (total unsaturated gases) yield was 30%, by mass, of the gas oil feedstock, and was produced using a non-catalytic heat carrier at 770 °C and 330 ms. Olefins, especially ethylene, propylene and butadiene, are valuable chemical intermediates used in the petrochemicals industry. Maximum yields of ethylene, propylene and butadiene from gas oil were 20.6, 7.3 and 3.1%, by mass, respectively. The use of catalyst had very little effect on olefin yields.

In general, the "coke" yields (i.e., the production of solid carbonaceous products) were relatively low, ranging from 0.5 to 6.5%, by mass, of the gas oil feedstock. Maximum coke yields are observed when maximum gasoline yields occur.

RESUME

Une étude préliminaire sur la transformation du gasoil en produits chimiques intermédiaires (i.e., oléfines, produits chimiques du pétrole) et en carburants pour le transport léger (i.e. essence) a été effectuée à l'unité pilote de Rapid Thermal Processing (RTP) d'Ensyn. L'unité a une capacité nominale d'un baril par jour, et est munie d'un nouveau réacteur qui permet un transfert de chaleur très rapide et des temps de séjour courts sur une vaste plage de température de réaction.

Neuf expériences ont été complétées pendant le projet. Parmi ces expériences, six comprennent un caloporteur non-catalytique (i.e., sable de silice) pour transférer la chaleur dans le réacteur. Pour les trois autres expériences, un caloporteur catalytique (i.e., un catalyseur de craquage d'aluminosilicate) a été utilisé. Des bilans de matière complets ont été effectués pour toutes les expériences de manière à vérifier les évaluations de rendements en produits.

Le rendement en essence non-optimisé le plus élevé a été de 16.2%, en masse, du stock d'alimentation en gasoil. Ce rendement a été obtenu en utilisant le caloporteur catalytique, à une température de 575°C et un temps de séjour de 500 millisecondes. Le rendement maximum (non-optimisé) en essence avec un caloporteur non-catalytique a été de 15.1%, et a été obtenu à une température de réaction de 840°C et un temps de séjour de 340 ms. L'utilisation d'un catalyseur a eu un effet important sur les rendements en essence à une température de réaction donnée.

Le rendement le plus élevé (non-optimisé) de la fraction évaporée et recueillie dans le décanteur a été de 25.8%, en masse, du stock d'alimentation en gasoil, lorsqu'un caloporteur catalytique à 670°C et 390 ms était utilisé.

Le rendement le plus élevé en oléfins (gaz non-saturés) a été de 30%, en masse, du stock d'alimentation en gasoil, et a été obtenu en utilisant un caloporteur non-catalytique, à 770°C et 330 ms. Les oléfins, surtout l'ethylène, le propylène et butadiène, sont des produits chimiques intermédiaires de grande valeur dans l'industrie pétrochimique. Les rendements maximum en éthylène, propylène et butadiène à partir du gasoil ont été, dans l'ordre, 20.6%, 7.3% et 3.1%, en masse. L'utilisation de catalyseur avait trés peu d'effet sur les rendement en oléfines.

En général, les rendements en «coke» (i.e., la production de solides carbonés) ont été peu élevés, soient entre 0.5% et 6.5%, en masse, du stock d'alimentation en gasoil. Les rendements maximum en «coke» sont observés lorsque les rendements en essence sont maximum.

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1.0 INTRODUCTION

There is an ever increasing interest in heavy petroleum feedstocks since oil prices are likely to rise again, light crude supplies are declining and there is a lower demand for residual oils. Gas oil in particular is an ideal candidate for upgrading, since it is a significant refinery byproduct. Suitable upgrading techniques must be developed to ensure that these heavy feedstocks are fully utilized. A number of upgrading processes are being investigated, among them is fast pyrolysis.

Fundamental laboratory-scale research in the early 1970s indicated that very high yields of valuable chemicals, chemical intermediates (i.e., the building blocks in the petrochemical industry) and fuels could be produced from a variety of carbonaceous materials under conditions of extremely rapid cracking. The fundamental research clearly indicated that both rapid heating of the feedstock material and precise control over a very short processing time are essential to achieve maximum yields of the desired products.

Conventional thermal processing equipment used in the petroleum, petrochemical and chemical industries cannot achieve the required rapid heating while still maintaining precise control over the necessary short processing time. Although many valuable petroleum, petrochemical and specialty chemical products are produced commercially in conventional equipment, a serious technical limitation exists which has prevented the optimization of yields, as well as the production of desirable fuels and chemicals from lower-grade feed materials.

The challenge in taking the promise of the fundamental research to a commercial concept was to engineer an innovative reactor system which could accomplish rapid heating of the carbonaceous feedstock while enabling precise control over the process reaction time. In the late 1970s, work began at the University of Western Ontario (U.W.O) to develop a fast pyrolysis process, termed Ultrapyrolysis. This concept used a hot heat carrier stream (inert gas and solids or simply inert gas) to transfer heat by direct contact with a variety of solid, liquid and gaseous carbonaceous feedstocks. A barrel and cone-shaped thermal mixer termed a "vortactor" was designed to rapidly heat the feedstock. The mixer was coupled to a tubular transport reactor which enabled the precise control of process time.

The Ultrapyrolysis program began under the ENFOR program (Environment Canada/Energy, Mines and Resources) with the intention of engineering a steady-state process to exploit the favourable fast pyrolysis product yields which were reported in bench-scale studies. Preliminary fast pyrolysis results using wood, cellulose and lignin in this system were encouraging, and are reported along with details of the design in a Federal Government report [1]. The relative success of the first phase of work led to a second phase of work sponsored by the Energy Project Office of the National Research Council of Canada (NRCC). The details of this study are also incorporated in a federal government publication [2]. The ability of the UP process to produce valuable chemical intermediates , such as ethylene, from the "model" carbonaceous feedstocks used, led to fast pyrolysis of heavy petroleum materials (i.e., pitch, tower bottoms, and heavy oil).

Although this work proved to be very promising and the results very reliable, limitations existed in the Ultrapyrolysis reactor design. Excessive wear or erosion of the reactor walls (when operating with a solid heat carrier) and "dead spots" of incomplete mixing had to be overcome, and provision made for scale-up to a commercial size. As a result, a Rapid Thermal Processing (RTP) pilot plant was designed and constructed at Ensyn's Ottawa facility. The new system was designed for durability and suitability for scale-up while still providing the critical conditions necessary for fast thermal processing (i.e., rapid thorough mixing and short contact times).

In an effort to continue the fast pyrolysis research which was started at U.W.O., Ensyn Engineering began an experimental program at its Ottawa facility. Initial work in the RTP system employed only sand as the heat carrier. Although preliminary results were promising for several applications, the next logical step in process development was to investigate the effects of various catalysts on product distributions. RTP is ideally suited for using a particulate catalyst since it can be directly substituted for the sand heat carrier. The catalyst then fulfils two roles; to carry heat, and to participate in the reaction kinetics. This study, co-sponsored by Canmet was carried out in the RTP system to investigate the rapid cracking of a representative gas oil, to yield lighter fuels and olefins. Both catalytic and non-catalytic fast pyrolysis of the gas oil were carried out. This report presents a summary of the project objectives, system description, and experimental procedures, results and conclusions.

2.0 PROJECT OBJECTIVES

The primary objectives of the, Rapid Thermal Processing (RTP) gas oil pyrolysis project are summarized as follows:

1. To prepare and modify the RTP system to accept a liquid petroleum feedstock and catalytic solid heat carrier.

2. To conduct preliminary tests to investigate the feasibility of using Rapid Thermal Processing to convert a representative gas oil to lighter fuels and valuable chemical intermediates.

3. To conduct four experiments; two at moderate temperatures (i.e., in the range of 550 to 650 °C) and at a residence time in the range of 200 to 500 ms; and two at high temperatures (i.e., 800 to 900 °C) and similar residence times, using a non-catalytic solid heat carrier (silica sand) and a catalytic solid heat carrier (silica/alumina cracking catalyst).

As is often the case with fundamental research programs, objectives are revised in response to periodic progress reviews during the course of the work. To allow a more complete comparison of the non-catalytic and catalytic experiments, additional runs were carried out. Nine experiments were conducted over a temperature range of 525 to 840 °C, (six non-catalytic, and three catalytic).

3.0 GENERAL ACCOMPLISHMENTS

Although there are a number of minor accomplishments which are natural byproducts of any fundamental research program (including development of new skills, new engineering and analytical techniques, training of personnel, and technology transfer), the principal unique accomplishments associated with the Canmet/Ensyn Rapid Thermal Processing (RTP) program may be summarized as follows:

1. Modifications to the equipment and system design changes were implemented with subsequent successful operation of the system using a liquid petroleum feedstock and catalytic heat carrier.

2. Preliminary gas oil pyrolysis experiments were conducted between 525 and 840 °C using both non-catalytic and catalytic solid heat carriers.

3. Preliminary interpretation of the general trends of the fast pyrolysis of gas oil as a function of temperature using a non-catalytic heat carrier.

4. Comparison of the product yield changes when using a non-catalytic and catalytic solid heat carrier.

5. Monitoring of the fractions of maltenes, asphaltenes and carbenes/carboids, which make up the liquid product.

6. Monitoring of the viscosity of the liquid product over the range of reaction conditions.

4.0 FLOW SCHEME AND EQUIPMENT

The existing RTP pilot plant, including its principal components, is illustrated in Figure 1. The plant is rated nominally at one barrel per day of liquid feedstock.

Hot solids (i.e., sand or catalyst) flow from a number of "heat carrier" feeders to the reactor system where they are injected into the rapid thermal mixer. The carbonaceous feed material (solid, liquid, or gaseous) is delivered from one of several interchangeable feeders (i.e., the "liquid feeder" in the present configuration) to the top of the reactor where it is injected into the cloud of turbulent hot solids. Extremely rapid heating of the feed material is achieved as the feed and hot solid heat carrier particles are quickly and thoroughly mixed. After the fast, intimate mixing is complete, the feed and solid heat carrier pass through a tubular transport reactor, the length of which is adjusted to control the processing (residence) time.

The products are rapidly cooled in a transfer line after the hot solids are removed in a solids "catch pot" or drop-out vessel. Additional cooling is carried out in the primary (water-cooled) and secondary (dry ice/acetone-cooled) condensers, where condensation of vapours and recovery of liquids also occur. The aerosol exiting from the condenser flows to an electrostatic precipitator (see Appendix 10.1 for design details). Approximately 95% of the aerosols are recovered in the precipitator, which operates at about 20 kV. Parallel filters are used to collect persistent aerosols, and the clean gas is then directed

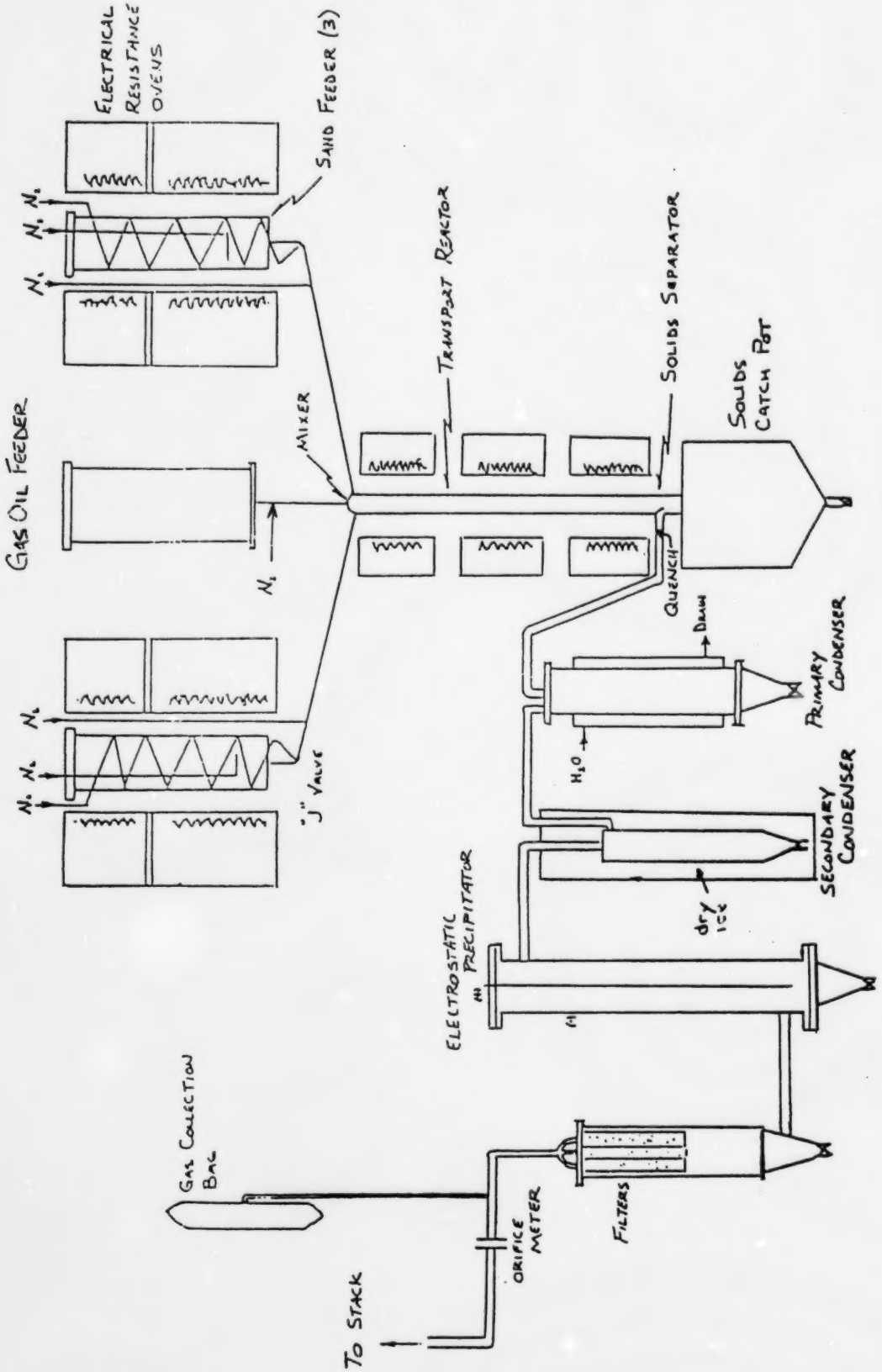


Figure 1. RTP Pilot Plant Schematic

through an orifice meter (to quantify the flow for mass balance closure). A fractional quantity of the product gas is continuously "bled" from the main stream to a gas sample bag for subsequent analyses.

There are three identical heat carrier feeders which serve to heat up the solid heat carrier and deliver it to the transport lines. Each feeder is about 1.2 m long and 150 mm outside diameter (Sch 40 pipe; 6" nominal diameter), and can hold 30 kg (silica sand). The maximum feed rate is about 60 kg/h (for each feeder) and the maximum temperature 1000 °C. Feeder control is accomplished via a sparger tube and a non-mechanical, high temperature "J" valve.

The gas oil feedstock is injected into the reactor using a pressurized, pneumatic-nozzle atomization design. A schematic diagram of the atomization system is illustrated in Figure 2, and a summary of the design parameters included in Table 1. Since the gas oil feedstock does not readily flow at room temperature, heating to about 50 °C prior to transport was required. The entire oil reservoir and atomization system is housed in a convection oven.

The reactor system consists of a rapid thermal mixer and two lengths of transport reactor - each of these having independent temperature control. Rapid mixing of the feedstocks with the solid heat carrier takes place in the rapid thermal mixer, and chemical reactions are then allowed to proceed in the transport reactor sections. The reactor is 1.2 m in length and is the constructed of Sch 40 Inconel 601 (40 mm I.D./1.5" nominal).

The solids catch pot is an inertial separator constructed of stainless steel and can hold about 100 kg of hot solids. Separation of the gases from the solids is based on the lower momentum of the gas-vapour product (compared to

Table 1. Feedstock Injection System Design Parameters

FEEDSTOCK RESERVOIR	
Capacity	0.8 litres
Height	2.2 m
Outside Diameter	3" Type K copper water pipe
Flange Thickness	3.2 mm
Flange Diameter	127.0 mm
Material of Construction (Flanges)	copper
INJECTOR TRANSPORT TUBE AND NOZZLE	
Tube Outside Diameter	6.35 mm
Tube Wall Thickness	1.245 mm
Length	0.76 m
Material of Construction	Stainless Steel
Nozzle Inside Diameter	3.86 mm

the hot sand) which can change direction more readily than the solids, and escape into the transfer line to be quenched directly with nitrogen gas. When the system is operated at high temperatures, the cooling duty is substantial. The addition of further nitrogen quenching gas tends to dilute the product stream to a point where accurate analysis of the product gas is hindered. In order to resolve this dilution problem, a pneumatically-controlled sand feeder is installed to deliver room-temperature sand for cooling in place of the nitrogen. A simple reverse-flow cyclone is added prior to the primary condenser to remove the added particulate sand.

The primary condenser is a water-jacketed carbon steel pipe (having both an inner and outer water-jacket) which is lined with a chemical resistant paint. The cooling water enters the condenser at about 19 °C and cools the product to about 25 °C. The secondary condenser is also a lined, carbon-steel pipe which

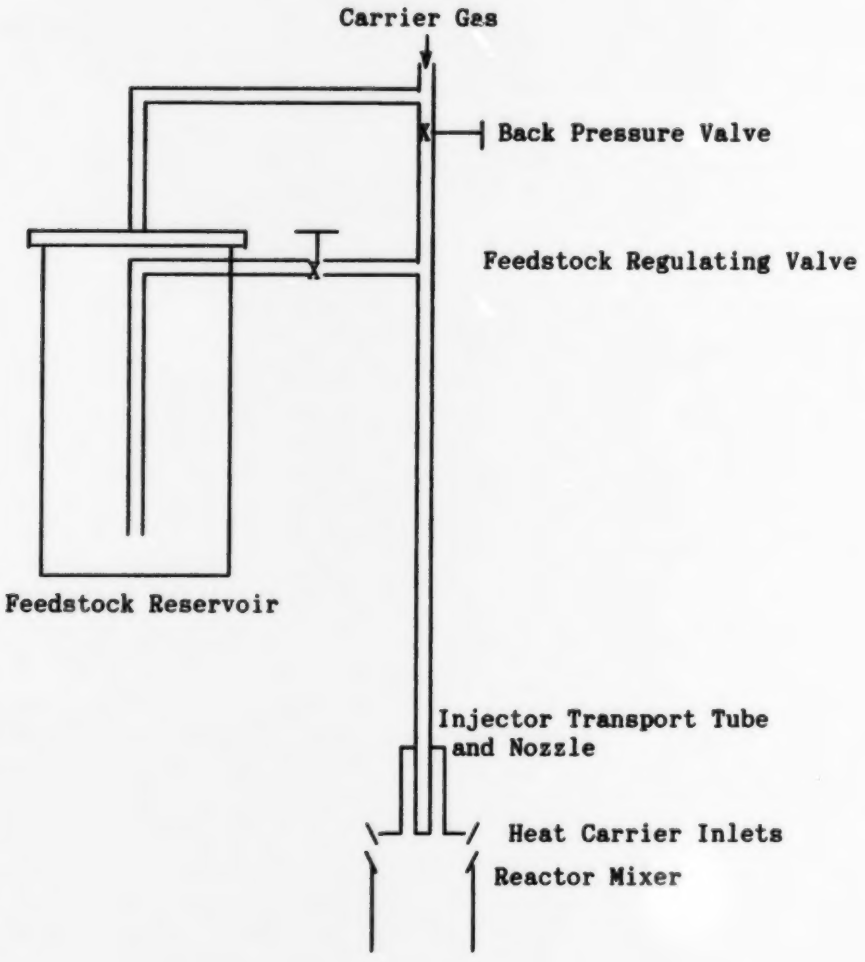


Figure 2. Schematic Diagram of Liquid Feedstock Injection System

is not jacketed but sits directly in an insulated dry ice box. It has a tangential gas/vapour inlet which forces the products to the condenser wall where efficient heat transfer can occur.

To ensure the removal of any entrained condensed liquid or fine solid residue, an electrostatic precipitator and a final filtration system are included in the product recovery stream. The electrostatic precipitator operates at 20 kV and is constructed of 7.6 cm (nominal 3 inch, sch 40) stainless steel pipe. The final filtration system consists of three parallel filters which are constructed of stainless steel, and have a pore size of 0.5 microns. They are housed in a single filter vessel. Each of these filter units are about 50 mm in diameter (outside) and about 0.5 m long.

All the system ovens were made "in-house", and are constructed of Watlow heaters, fiberfrax and duraboard insulation, and sheet metal cylinders. They are wired 3-phase and operate nominally at 220 volts.

5.0 FEEDSTOCK AND SOLID HEAT CARRIERS

5.1 Gas Oil Feedstock

Gas oil was supplied by Canmet (SUNCOR SF-135) and pyrolyzed during the experimental program. A summary of the feedstock characteristics, including elemental analysis, API gravity and viscosity is given in Table 2.

Table 2. Gas Oil Data Sheet

ELEMENT	WEIGHT PERCENT
Carbon	87.50
Hydrogen	11.90
Sulphur	0.77
Nitrogen	0.10
PHYSICAL PROPERTIES	
Density @ 15 °C	928.3 kg/m^3
API gravity	20.72
Viscosity @ 40 °C	26.0 centistokes
Molecular Weight	310 kg/kgmole
Mean Average Boiling Point MeABP	381.9 °C
Watson Characterization Factor	11.38

5.3 Solid Heat Carriers

5.3.1 Non-Catalytic Solid Heat Carrier

The non-catalytic solid heat carrier was simply F-40 grade non-porous silica sand supplied by Indusmin, St. Canut, Quebec. The mean diameter particle size is 256 μm and the moisture content less than 0.5% by mass. Other physical properties and the size analysis are summarized in Table 3.

Table 3. Solid Heat Carrier (Silica Sand) Characterization

SIEVE SIZE (microns)	MEAN PARTICLE Size Dp(I)	WEIGHT (g)	WEIGHT PERCENT W(I)	CUMULATIVE WEIGHT PERCENT	W(I)/Dp(I)
589	711	0.7	0.7	100.0	0.000984
417	503	10.9	10.9	99.3	0.021669
295	356	33.2	33.2	88.4	0.093258
208	251.5	35.1	35.1	55.2	0.139562
147	177.5	14.8	14.8	20.1	0.083380
104	125.5	3.9	3.9	5.3	0.031075
74	89	1.1	1.1	1.4	0.012359
pan	37	0.3	0.3	0.3	0.008108
		100.0	100.0		0.390399

Maximum Particle Size = 833 μm
Sauter Mean Diameter = 256.15 μm
Uncompacted Density = 1390.0 kg/m^3

Chemical Analysis

SiO_2	99.60
Fe_2O_3	0.06
Al_2O_3	0.24
CaO	0.04
LOI*	0.07

* LOI - loss on ignition.

5.3.2 Catalytic Solid Heat Carrier

The catalytic solid heat carrier was DA-440 cracking catalyst supplied by W.R. Grace Company, Valleyfield, Quebec. The catalyst has a mean particle diameter of 69 microns and an activity of 83%. Other specifications are given in Table 4.

Table 4. DA-440 Catalyst Data Sheet

Density @ 15 °C	850.0 kg/m^3
Pore Volume	0.35 cc/g

Chemical Analysis	
SiO_2	45.2
Fe_2O_3	0.56
Al_2O_3	44.2
Na	0.44
LOI*	7.8

* LOI - loss on ignition.

The loss on ignition of the fresh catalyst heat carrier was determined experimentally, and is summarized in Appendix 10.2.

6.0 RTP EXPERIMENTAL PROCEDURE

6.1 RTP Pyrolysis Experimental Procedure

The furnaces which house the heat carrier (i.e., sand or catalyst) feeders, mixer and the reactor are activated about 8 hours prior to an experiment. The solid heat carrier feeder ovens are set at a temperature which is about 100 to 150 °C greater than the desired reaction temperature. This temperature differential accounts for transport/reactor system thermal losses and provides the heat required to raise the feedstock from ambient to reaction temperature.

During the heat-up period, a number of system checks, calibrations and peripheral system activations are carried out:

- the gas chromatograph is turned on, brought to desired operating conditions, and calibrated using a known gas sample;
- the system is pressure-tested to detect and correct any leaks;
- nitrogen is allowed to continually purge the system of air and residual product gas;
- water is fed to the primary condenser water-jacket;
- the secondary condenser bath is filled with dry-ice;
- the gas sampling bag is purged and evacuated;
- the chart recorder for reactor temperatures is activated;
- computer programs are run to assist in setting the carrier gas flows (these allow selection of the desired residence time as a function of temperature and reactor volume).

Just prior to the beginning of the experiment, the following steps are taken:

- the quench gas (which cools the product stream) is delivered to the gas exit line;
- system transport gas (nitrogen) flow is initiated in the "bypass" mode;
- transport gas is delivered to the heat carrier feeders and the feeder vibrators are activated;
- the feeder transport gas is diverted to the heat carrier feeder, and solids flow is verified using a thermocouple;
- fluidization gas in the heat carrier feeding mechanism is adjusted until the desired reactor inlet temperature is reached;
- the reactor temperatures are monitored on the chart recorder to ensure that the desired setpoint has been realized.

The actual experiment begins when the liquid feedstock feeder is activated and the oil is delivered to the reactor system. At this point, the gas sampling bag valve is opened and a constant flow of product gas is bled from the main gas line to the gas bag. Orifice measurements for determining gas flow are taken every 30 seconds. System temperatures, gas flows (via rotameters and an orifice meter) and pressures are monitored continually.

Solid heat carrier flowrates are adjusted as required, to maintain the desired reactor temperatures and to ensure isothermal conditions. After the desired quantity of oil has been fed, the steady-state experiment is terminated when the oil feeder regulating valve is closed. The data recorders, system furnaces and carrier gas flows are then shut down (the quench gas is the last transport gas flow to be turned off). After product collection and analysis (described in the following sections), the equipment is reassembled and feeders are charged with fresh solid heat carrier or gas oil in preparation for the next experiment.

6.2 Gas Analysis

At least three gas samples are taken from the sampling bag and analyzed for hydrogen, carbon monoxide, carbon dioxide and C1 to C6 using a Carle 400 series refinery gas chromatograph coupled to a Spectra Physics 4290 integrator. The C5/C6 fraction is analyzed as a single constituent. After gas analyses, the quantity of sampled gas is determined by evacuation into a vacuum tank of known, fixed volume. The total mass of the gas is then determined using the ideal gas law (i.e., it is assumed that the nitrogen and product gases behave ideally):

$$PV = nRT = mRT/M$$

P - absolute pressure of the gas
V - volume of the gas
n - number of moles of the gas
R - universal gas constant
T - absolute temperature of the gas
m - mass of the gas
M - average molecular weight of the gas

As the gases are evacuated into the tank, the change in pressure (ΔP) can be measured and related to the change of gas mass within the vessel. This change in mass is simply the mass of the product gas (m_p):

$$m_p = \Delta PVM/RT$$

The absolute temperature is easily determined, the average molecular weight of the gas is calculated from the analysis, the tank volume is accurately known and the gas constant is known. Therefore the gas mass in the bag can be calculated. From the bag gas mass and the G.C. gas analysis, the mass yield is determined for each gas component.

Data which is recorded during the experiment (i.e., temperatures, pressures, rotameter readings, etc.) is entered, along with the results of the gas analysis, into a personal computer (PC). The computer calculates the reactor residence time and the yields of gas going through the orifice meter and the amount collected in the sample bag (by the method described above) and gas components. It then prints out a systematic summary of the operating conditions, experimental data and product yields (mass balance). A sample output from a gas oil pyrolysis experiment is given in Appendix 10.3.

6.3 Pyrolysis Liquid Recovery and Analysis

The product recovery system (catch pot, cyclones, condensers, filters, transport lines, etc.) is disassembled and flushed with an appropriate solvent to recover pyrolytic liquids. THF was used for the product recovery in the first two experiments. However, acetone, which is considered to be a safer solvent, was found to work just as well. For the remaining experiments acetone was therefore used as the cleaning solvent. Solids which have been collected with the liquids (i.e., the small fraction which has not been collected in the solids catch pot) are filtered from the solvent, quantified by gravimetry and then ashed for char determination. The filtered mixture of pyrolytic liquid and solvent is rotary-evaporated to recover and quantify the raw liquid product.

The quality of the liquid product is assessed by determining the standard liquid fractions - maltenes, asphaltenes and carbenes/carboids. This type of analysis and characterization is carried out by a series of solvent extractions. Maltenes are extracted first from the product using n-pentane and represent the

lightest liquids. These are considered to be of higher value than the increasingly heavier asphaltenes and carbenes/carboids. The former fraction is soluble in toluene while the latter is the insoluble residue.

During the experimental program the standard fractions were determined using a 500 ml Soxhlet extraction apparatus from Canadawide Scientific (model 4215-06). In this apparatus, the solvent is refluxed until it is certain that the entire fraction has been dissolved.

After cooling in the inert atmosphere of the catch pot (to prevent combustion when exposed to air), the bulk recovered solids are riffled, sampled and ashed to determine the solid residue (i.e., coke) yield. Ashing is carried out (on the samples and a sand "control") in a muffle furnace according to ASTM procedures.

6.4 Solid Residue Determination

The solid carbonaceous residue or "coke" produced from gas oil during an experiment is deposited along with the solid heat carrier either in the solids catch pot or the downstream recovery equipment. Most of the solids, however, remain in the catch pot. Representative samples must therefore be taken from both of these locations in order to determine the yield of solid residues, and to carry out the mass balance procedure.

When sand is used as the heat carrier, the coke residue determination is straightforward. In the catch pot, the solids are cooled in an inert nitrogen atmosphere after an experiment in order to prevent combustion of the carbonaceous

residue in the presence of air. The cooled solids are then riffled, sampled, dried (at 105 °C), and ashed. The ashing procedure, used to determine the carbonaceous residue yield, is carried out in a muffle furnace using ASTM method D3174 as a guide. Clean sand samples (or "blanks") are taken from the heat carrier feeders after a run, and are then dried and ashed (ASTM D3174) to determine what correction, if any, must be made for catalyst "loss on ignition".

The heat carrier and carbonaceous solids, which are recovered in the downstream equipment, are separated from the liquids by filtration. These solids are then dried and ashed according to the ASTM procedure referenced above.

When catalyst is used as the heat carrier, another method must be developed for "coke" determination. Since the catalyst is porous and has a large surface area, a considerable amount of water (and other liquids) can strongly adsorb to the catalyst surfaces. This water is known as hydrated water, and is not eliminated by drying procedures carried out at 105 °C (only free surface water is eliminated under such conditions). Hydrated water will, however, be driven off when exposed to the high temperatures associated with ashing. Therefore, if the coke determination procedure (drying at 105 °C followed by ashing), which was developed for sand, is applied to the catalyst, hydrated water will be driven off along with the carbonaceous material during ashing. The resultant estimate of coke will be much higher than the real value.

To overcome this limitation, a three-stage method for coke determination was developed for experiments using a catalyst heat carrier. First, the riffled representative sample is dried in a convection oven at 105 °C for two to three hours to drive off the free water. The sample is then heated to 500 °C in an

inert nitrogen atmosphere for two to three hours to determine the hydrated water content. Without oxygen, no coke is eliminated during this second stage. Finally, the catalyst is ashed, in a manner similar to that used for sand, to determine the carbonaceous residue. A "blank" catalyst sample is removed from the heat carrier feeder and then ashed to determine whether any correction should be made to the coke yield estimate.

7.0 RESULTS

7.1 Overview

The original objective of the project was to conduct four experiments in the RTP system. Two experiments (one non-catalytic and one catalytic) were to be carried out at a moderate temperature between 600 and 700 °C, and within the residence time range of 300 to 500 ms. Two corresponding experiments (non-catalytic and catalytic) were to be carried out at a higher temperature, between 800 and 900 °C, and within a similar range of residence times. The actual experimental program went beyond the scope of the proposed work plan. A total of nine experiments were completed. Six of these were non-catalytic runs and three were catalytic. The maximum reactor temperature for the catalytic runs was restricted to 825 °C because of the thermal limits of the zeolite catalyst [4]. At temperatures above 825 °C, the zeolite structure is destroyed and the catalyst is deactivated.

This chapter is divided into several sections which include a comparison of experiments using a non-catalytic and heat carrier. The sections deal sequentially with the following topics:

- mass balance and overall yields of gas, liquid and coke;
- gas component and liquid fraction yields, and overall conversion;
- the effect of heat carrier on the liquid fractions (maltenes, asphaltenes and carbenes/carboids);
- the viscosity of the liquid product from selected experiments.

7.2 Mass Balance and Product Yields

A total of nine gas oil pyrolysis experiments were conducted during the preliminary experimental program. A summary of the product yields and mass balance closure is given in Table 5. The reported liquid yields have been corrected for the presence of any solvent after analysis at the Canmet laboratory. A summary of all analyses performed at the Canmet laboratory is given in Appendix 10.4. The solid residue (i.e., coke) results reported in the table represent the corrected yields obtained experimentally as outlined in Chapter 6.3. A summary of the yields of solid residue found in the "downstream" recovery equipment and catch pot as determined in the RTP laboratory is given in Table 6. The majority of coke typically ends up in the downstream recovery equipment. This is becasue of the inability of the catchpot to remove the light coke along with the solid heat carrier. A summary of the uncorrected solid residue determination by Canmet is given in Table 7. In the case of the Canmet results, the solid residue yields were found to be quite high, representing almost 50 wt% of the feed for the catalytic heat carrier experiments. Since this would cause the mass balance to fall well above 100 %, it is obvious that some correction is necessary.

The mass balance ranged from 93.7 to 112.1 %, with the exception of CGO-7. During the recovery procedure of CGO-7, some of the liquids were lost when the roto-evaporator round bottom flask was broken. To "normalize" the product distribution, the gas and coke yields were taken as correct and the liquid yield determined "by difference". This approach is assumed to be valid

Table 5. Rapid Thermal Processing of Gas Oil: Product Yield Summary and Mass Balance

RUN NO.	REACTION TEMPERATURE (C)	RESIDENCE TIME (ms)	SOLID HEAT CARRIER (g)	GAS OIL FED (g)	PRODUCT YIELD Total Gas (g)	(%)	Total Liquid* (g)	(%)	Solid Residue (g)	(%)	PERCENT CLOSURE
[s]CGO-1	600	350	27475	485	23.2	4.8	440.0	90.7	2.5	0.5	96.0
[s]CGO-2	525	400	17980	640	4.1	0.6	605.0	94.5	7.9	1.2	96.4
[s]CGO-3	600	520	44820	340	48.4	14.2	280.0	82.4	6.2	1.8	98.4
[s]CGO-4	770	330	50935	190	91.8	48.3	110.0	57.9	10.0	5.2	111.4
[s]CGO-5	840	340	30475	110	58.6	53.3	57.6	52.4	7.1	6.5	112.1
[c]CGO-6	575	500	4650	63	16.2	25.7	40.0	63.5	4.1	6.5	95.7
[s]CGO-7	675	355	50965	195	37.1	19.0	100.0	51.3	9.3	4.8	75.1
[c]CGO-8	770	492	29450	130	54.2	41.7	60.0	46.2	7.8	6.0	93.8
[c]CGO-9	670	390	12525	150	39.4	26.3	94.0	62.7	7.2	4.8	93.7

Table 6. Rapid Thermal Processing of Gas Oil: Summary of the Solid Residue Found in the Downstream Recovery Equipment and Catch Pot as Determined at the RTP Laboratory.

RUN	DOWNSTREAM RECOVERY EQUIPMENT FRACTION OF COKE	SAMPLE (g)	COKE (g)	CATCH POT FRACTION OF COKE	SAMPLE (g)	COKE (g)	TOTAL (g)
[s]CGO-1	.00155	1625	2.52	negligible	25850		2.52
[s]CGO-2	.0039	2020	7.88	negligible	15960		7.88
[s]CGO-3	.00205	1320	2.71	.00008	43500	3.48	6.19
[s]CGO-4	.0064	1555	9.95	negligible	49380		9.95
[s]CGO-5	.0044	1615	7.11	negligible	28860		7.11
[c]CGO-6	.074	55	4.07	negligible	4595		4.07
[s]CGO-7	.037	250	9.25	negligible	50715		9.25
[s]CGO-8	.0085	580	4.93	.0001	28870	2.89	7.82
[s]CGO-9	.04	55	2.20	.0004	12470	4.99	7.20

Note: 1. The sand heat carrier run samples were corrected for the inherent loss on ignition of the sand itself (averaging 0.033 wt%).

2. The catalyst heat carrier experiment samples were ashed according to the procedure outlined in Chapter 6.

s represents experiments in which sand was the solid heat carrier
c represents experiments in which catalyst was the solid heat carrier

Table 7. Rapid Thermal Processing of Gas Oil: Summary of the Solid Residue Found in the Recovery Equipment and Catch Pot as Determined at the Canmet Laboratory.

RUN	DOWNSTREAM RECOVERY EQUIPMENT			CATCH POT			TOTAL
	FRACTION OF COKE	SAMPLE (g)	COKE (g)	FRACTION OF COKE	SAMPLE (g)	COKE (g)	(g)
[s]CGO-1	.0013	1625	2.11	.0004	25850	10.34	12.45
[s]CGO-2	.0033	2020	6.67	.0002	15960	3.19	9.86
[s]CGO-3	.0017	1320	2.24	.0002	43500	8.70	10.94
[s]CGO-4	.0044	1555	6.84	.00011	49380	5.43	12.27
[s]CGO-5	.0033	1615	5.32	.0002	28860	5.77	11.09
[c]CGO-6	.0624	55	3.43	.0078	4595	35.84	39.27
[s]CGO-7	.011	250	2.75	.0003	50715	15.21	17.96
[c]CGO-8	.099	580	57.42	.001	28870	28.87	86.29
[c]CGO-9	.0337	55	1.85	.0022	12470	27.43	29.28

s represents experiments in which sand was the solid heat carrier

c represents experiments in which catalyst was the solid heat carrier

since the liquid portion of the product is the most difficult to collect and recover. The large surface area of recovery equipment must be washed with solvent, and the solvent subsequently separated from the liquid products using roto-evaporation equipment. Not only can there be losses during the washing stage, but during roto-evaporation some of the lighter liquids can be evaporated with the solvent. The gas yield is considered to be quite accurate as previous calibration and tracer study experiments have shown. Since the solid residue represents the smallest product yield, relative to the gas and liquid yields, a small error in its determination will have little effect on the overall mass balance. Thus, the approach of taking the liquid yield "by difference" is reasonable.

A summary of the normalized product yields is given in Table 8. From this table, a plot of yield versus temperature for the non-catalytic heat carrier

experiments (residence time range of 330 to 492 ms) is shown in Figure 3. The gas yield was found to increase asymptotically as the temperature increased, while the liquid yield was found to behave inversely to the gas yield. As the temperature increased, the liquid yield decreased asymptotically. The solid residue yield increased gradually over the temperature range of investigation, but can be considered to be relatively constant (at about 6 wt%) between 675 and 840 C. The maximum gas yield was found to be 53.3 wt% of the feed at 840 C, while the maximum liquid yield of 98.1 wt% occurred at 525 C.

Table 8. Rapid Thermal Processing of Gas Oil: Normalized Product Yield Summary

RUN NO.	REACTION TEMPERATURE (C)	RESIDENCE TIME (ms)	GAS OIL FED (g)	PRODUCT YIELD TOTAL GAS (g)	(%)	TOTAL LIQUID+ (g)	(%)	SOLID RESIDUE (g)	(%)
[s]CGO-1	600	350	485	23.2	4.8	459.3	94.7	2.5	0.5
[s]CGO-2	525	400	640	4.1	0.6	628.0	98.1	7.9	1.2
[s]CGO-3	600	520	340	48.4	14.2	285.4	83.9	6.2	1.8
[s]CGO-4	770	330	190	91.8	48.3	88.3	46.4	10.0	5.2
[s]CGO-5	840	340	110	58.6	53.3	44.3	40.3	7.1	6.5
[c]CGO-6	575	500	63	16.2	25.7	42.7	67.8	4.1	6.5
[s]CGO-7	675	355	195	37.1	19.0	148.6	76.2	9.3	4.8
[c]CGO-8	770	492	130	54.2	41.7	68.0	52.3	7.8	6.0
[c]CGO-9	670	390	150	39.4	26.3	103.4	68.9	7.2	4.8

+ Liquid yield found by difference
s represents experiments in which sand was the solid heat carrier
c represents experiments in which catalyst was the solid heat carrier

In Figure 4, the product yields using a catalytic heat carrier have been included together with the non-catalytic heat carrier curves. At lower temperatures the gas yield is much higher for catalytic heat carrier pyrolysis. As the temperature increases, however, the product yields of gas, liquid, and coke approach that of the non-catalytic heat carrier results. This is likely due to the destruction of the zeolite catalyst, since it must be heated to temperatures in excess of 825 C to obtain a reactor temperature of 770 C [4].

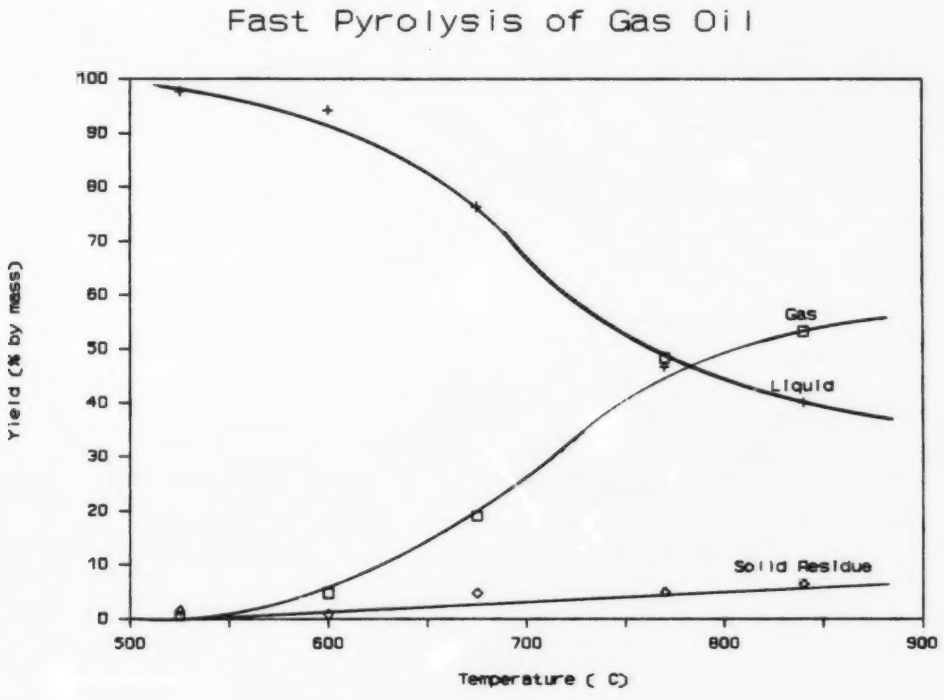


Figure 3. **Gas Oil Pyrolysis using a Non-Catalytic Solid Heat Carrier: Product Yields vs Temperature.**

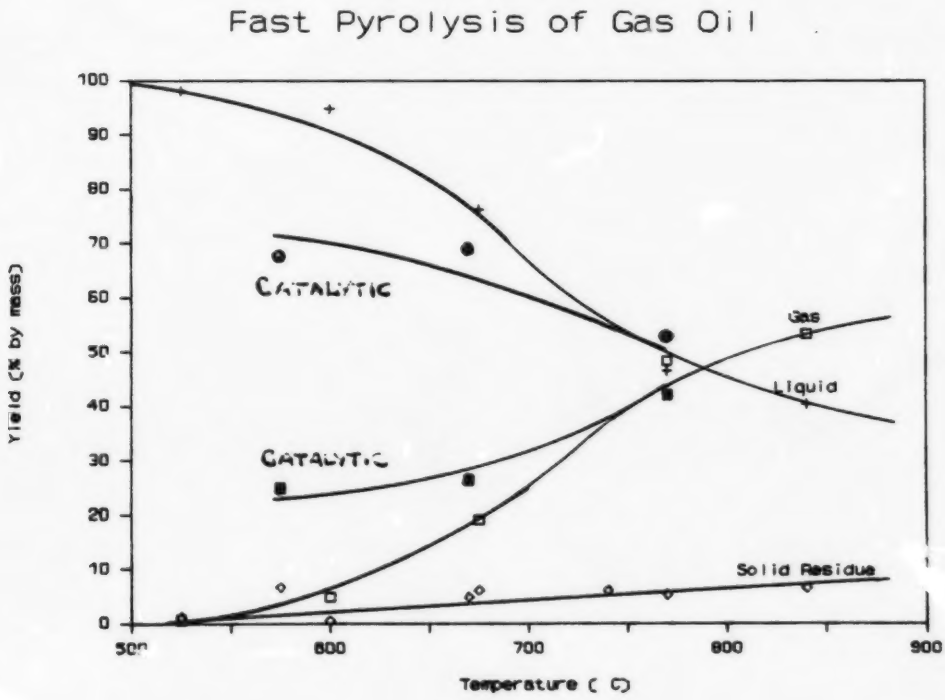


Figure 4. **Gas Oil Pyrolysis Using Both a Catalytic and a Non-Catalytic Heat Carrier: Product Yields vs Temperature.**

7.3 Component Yields

From the gas analysis performed at the Ensyn laboratory and the liquid analysis completed at Canmet (Appendix 10.4), a summary of the gas component yields and liquid fractions was prepared (Table 9). The calculations which were carried out to obtain the liquid fractions from the Canmet analyses is summarized in Appendix 10.5.

Table 9. Rapid Thermal Processing of Gas Oil: Summary of the Normalized Component Product Yields.

REACTION CONDITIONS	CGO-1	CGO-2	CGO-3	CGO-4	CGO-5	CGO-6	CGO-7	CGO-8	CGO-9
Temperature (C)	600	525	600	770	840	575	675	770	670
Residence Time (ms)	350	400	520	330	340	500	355	492	390
Heat Carrier	sand	sand	sand	sand	sand	catalyst	sand	catalyst	catalyst
PRODUCT YIELDS (% by mass)									
Hydrogen			0.02	0.10	0.92			0.64	0.12
Ethylene	0.96	0.07	2.82	16.58	20.64	0.94	6.63	15.23	5.05
Ethane	0.22	0.03	0.81	1.57	0.83	0.18	1.40	1.08	0.95
Acetylene				0.29	1.37		0.05	0.86	0.50
Methane	0.43	0.03	1.43	8.57	12.60	0.39	4.13	9.06	3.23
Carbon Dioxide	0.21	0.12	0.47	0.71	0.88	0.52	0.02	0.17	0.06
Hydrogen Sulphide			0.04	0.05	0.29	0.84		0.13	1.65
Propane	0.04		0.14	0.26	0.04	0.94	0.17	0.14	0.46
Propylene	0.80	0.06	2.57	7.28	3.38	4.99	3.52	4.64	7.53
Butene-1	0.25		0.76	0.92	0.07	1.03	0.73	0.92	1.30
Isobutylene	0.14		0.46	0.98	0.17	1.89	0.67	0.58	1.87
Trans-Butene-2	0.04		0.15	0.18		1.19		0.34	1.01
Cis-Butene-2			0.11	0.40	0.49	0.94		0.57	0.78
Butadiene	0.14		0.47	3.08	1.87	0.38	0.86	2.04	0.59
Total Gas	3.23	0.31	10.25	40.97	43.26	14.23	18.18	36.40	25.10
C_5/C_6	1.54	0.33	4.00	7.36	9.71	12.17	0.86	5.07	0.99
Gasoline (incl. C_5/C_6)	4.48	2.29	8.24	11.44	15.07	16.24	8.63	12.13	11.04
216-343 C Fraction	25.57	22.56	24.43	14.48	10.92	16.61	27.43	19.93	25.84
343 C + Fraction	66.20	73.58	54.43	27.84	24.02	47.12	41.91	25.31	33.00
Coke	0.5	1.2	1.8	5.2	6.5	6.5	4.8	6.0	4.8
Conversion*	8.24	3.86	21.14	57.68	65.06	36.27	30.66	54.76	41.16

* as requested by the Scientific Authority, conversion is defined as 100 - (LCO + DO)

The yields of total gas (i.e., light noncondensible gases) were found to differ very little when using either a non-catalytic or catalytic heat carrier under similar reactor conditions (i.e., similar temperature and residence time). The yields of these light noncondensible gases are expected to consistently increase to a maximum as the residence time is increased at a given temperature. Comparing CGO-1 and CGO-3, a 170 ms increase in residence time leads to a significant increase in the noncondensible gas yields. At 840 C, the yield of ethylene, propylene, and butadiene exceeded 20.6, 3.4 and 1.9 % by mass of the feedstock, respectively. During one experiment using sand as the heat carrier (CGO-4), a propylene yield of approximately 7.3 % by mass of the feedstock was observed. Ethylene, propylene and butadiene are considered to be particularly useful as petrochemicals. The production of these petrochemicals from gas oil would not be enhanced using the zeolite catalyst employed during this project. The zeolite appears to favour other products. Comparing CGO-7 and CGO-9, the yield of ethylene is less (by more than 1.5 %, by mass, of the feed) when a catalyst heat carrier is used than when a sand heat carrier is used under similar conditions. The hydrogen sulphide and hydrogen yields, however, are significantly higher when the catalyst heat carrier is employed.

The yield of C_3 and C_4 are higher at lower temperature in the case of catalytic cracking. Comparing CGO-7 and CGO-9, the C_3/C_4 yield from CGO-9 was 13.5 % by mass of the feed compared with 6.0 % by mass of the feed for CGO-7. At higher temperatures (e.g., CGO-8) the quantity of C_3 and C_4 actually decreased because of the increased cracking under the more intense reactor conditions.

The gasoline yield (C_5+) was found to be the highest (16.24 % of the feedstock mass) for experiment CGO-6 (575 C, 500 ms, catalytic heat carrier). The next

highest gasoline yield (15.1 % of the feedstock mass) was for experiment CGO-5 (840 C, 340 ms, sand heat carrier). At higher temperatures, the use of a catalytic heat carrier (CGO-8, and CGO-9) results in a much lower gasoline yield (12.13, and 11.04 % by mass of the feed).

The conversion was defined by the Scientific Authority (Dr. Ng) as follows:

Conversion = 100 - (LCO + DO)

where, LCO = the percentage of liquid product boiling in the range of 216 to 343 C
DO = the percentage of liquid product boiling above 343 C

The highest conversion was 65.1% for experiment CGO-5 on which a sand heat carrier was used at a temperature of 840 C and a residence time of 340 ms. In general, the conversion observed during experiments conducted at lower temperatures, was higher when a catalytic heat carrier was used (under otherwise similar reaction conditions). At higher temperatures the use of a catalytic or non-catalytic heat carrier had little effect on conversion.

The coke yield was found to increase from 1.2 to 6.5 % by mass of the feed with an increase in reactor temperature from 525 to 840 C. The coke yield for the catalytic experiment conducted at a lower temperature (CGO-6) was considerably higher than for the comparable sand run (CGO-3). At higher temperatures, the coke yield for both the catalytic and non-catalytic pyrolysis experiments was similar.

7.4 Soxhlet Extraction Results

The analytical results from the standard fractions of the liquid product are given in Table 10. These numbers represent the average values from the

analytical results presented in Appendix 10.6. The quality of the product, as assessed by the maltenes content (wt%), was much lower than that of the gas oil feedstock, while the carbenes/carboids content was substantially higher. Fast pyrolysis therefore appears to consist of the cracking of the lighter liquid fractions to light gases and vapours while rejecting carbon to the carbenes/carboids fraction. The fraction of maltenes in the liquid product from high-temperature experiments was found to be considerably lower than that of lower temperature pyrolysis. Comparing CGO-2 with CGO-5, the maltenes fraction drops from 57.94 to 3.56 % by mass of the liquid product as the temperature increases from 525 to 840 C. The effect of a catalytic heat carrier on the maltenes content of the liquid product is illustrated in a comparison of CGO-6 (catalytic heat carrier) and CGO-3 (non-catalytic heat carrier). In the case of the catalytic pyrolysis experiment, the lighter maltenes fraction of the liquid product was cracked in favour of a gaseous/vapour product.

Table 10. Rapid Thermal Processing of Gas Oil: Standard Fractions of the Feedstock and Liquid Products.

Sample	Temperature (C)	Res. Time (ms)	Maltenes	Asphaltenes	Carbenes/Carboids
			(wt% of the liquid)		
[s]CGO-1	600	350	53.48	9.34	37.18
[s]CGO-2	525	400	57.94	3.87	38.19
[s]CGO-3	600	520	50.56	15.44	34.0
[s]CGO-4	770	330	8.92	16.25	74.84
[s]CGO-5	840	340	3.56	13.25	83.19
[c]CGO-6	575	500	55.17	11.43	33.41
[s]CGO-7	675	355	14.85	33.18	51.96
[c]CGO-8	770	492	7.33	45.75	46.92
[c]CGO-9	670	390	17.92	33.84	48.24
Feedstock			83.39	14.30	2.31

s represents experiments in which sand was the solid heat carrier
c represents experiments in which catalyst was the solid heat carrier

7.5 Liquid Product Viscosity

The viscosity of the liquid product for the first six experiments was examined using a Fisher Tag Viscometer. Not enough sample was available to perform a viscosity check on the last three experiments. A summary of the results is given in Table 11. Comparing the average kinematic viscosity with that of the gas oil feedstock (26.0 centistokes), there is a significant reduction in the viscosity of the liquid products. Comparing individual experiments, it appears that as the temperature of reaction increased the viscosity of the liquid product decreased. Comparing the average viscosity of the liquid product to other petroleum fuels it would appear that the liquid product has similar characteristics to a No. 2 to No. 4 oil.

Table 11. Rapid Thermal Processing of Gas Oil: Summary of Liquid Product Viscosity

RUN NO.	REACTION TEMPERATURE (C)	RESIDENCE TIME (ms)	VISCOSITY (at 40 C) SAYBOLT UNIVERSAL (s)	KINEMATIC (cSt)
[s]CGO-1	600	330	79.0	15.7
[s]CGO-2	525	400	82.5	16.5
[s]CGO-3	600	520	67.5	12.5
[s]CGO-4	770	330	69.0	13.1
[s]CGO-5	840	340	60.0	10.5
[c]CGO-6	575	500	63.5	11.5

s represents experiments in which sand was the solid heat carrier

c represents experiments in which catalyst was the solid heat carrier

8.0 CONCLUSIONS AND RECOMMENDATIONS

8.1 Conclusions

This preliminary study indicated that relatively high yields of valuable gaseous chemical intermediates can be produced from the rapid pyrolysis of gas oil. In particular, high yields of ethylene, propylene, and butadiene can be realized at high temperatures using a non-catalytic solid heat carrier. At lower temperatures using a catalytic heat carrier the gasoline (C_5+) yield increases. In addition, at lower reactor operating temperatures the total non-condensible gas yield was found to be slighty higher when using a catalytic solid heat carrier.

From the analysis of the standard fractions of the liquid products it can be concluded that the fast pyrolysis of gas oil involves the cracking of the lighter, maltenes, fraction of the feedstock, producing lighter gaseous/vapour products with the rejecting of carbon in the form of carbenes/carboids and coke.

8.1 Recommendations

As a result of this preliminary study, a list of recommendations has been drafted to assist in directing and planning a more thorough investigation of the pyrolysis of gas oil:

1. Conduct a systematic study at temperatures above 800 °C using a non-catalytic solid heat carrier to characterize the chemistry and to optimize the production of valuable light chemical intermediates (i.e., ethylene, propylene, and butadiene).

2. Conduct a systematic fast pyrolysis study using a catalytic solid heat carrier at moderate temperatures to characterize the chemistry and to optimize the production of valuable liquid fuels and aromatics.

3. Conduct systematic studies using a catalytic solid heat carrier in which the heat carrier solid to feedstock loading is varied to investigate the effect on the product yields.

9.0 REFERENCES

1. Bergougnou, M.A., H.I. de Lasa, L.K. Mok, R.G. Graham, B.A. Freel and J.D. Hazlett. Ultrapyrolysis of Cellulose and Wood Components. Enfor C-147 Final Report. Environment Canada. Ottawa, Canada (1983).

2. Bergougnou, M.A., R.G. Graham, B.A. Freel and L. Vogiatzis. An Investigation of the Fast Pyrolysis of Cellulose and Wood. Final Report. NRC Canada. Ottawa, Canada (1985).

3. Speight, J.G. The Chemistry and Technology of Petroleum. Marcel Dekker, New York, (1980).

4. Letzsch, W.S., R. E. Ritter, and D.E.W. Vaughan. "Lab can evaluate zeolite FCC catalyst", Oil and Gas Journal, Vol 74-4. pp. 130-144. (1976).

10.0 APPENDICES

10.1 Electrostatic Precipitator Design

10.1 Electrostatic Precipitator Design

The electrostatic precipitator (EP), illustrated in Figure 10.1, was sized to ensure that there would be sufficient time for a charged particle to migrate from the centre of the unit to the collection cylinder.

The typical superficial velocity of the gas/vapour phase within an EP should be about 1 m/s or less to avoid reentrainment of the collected particles [1,2]. Thus the collection cylinder specified in the design must have a cross-section which allows a gas/vapour superficial velocity of about 1 m/s.

The EP diameter was determined on a "worst case" basis, by assuming the maximum volumetric flow of material through the device. From prior studies it was determined that the maximum flow would be:

$$\text{Max. Vol. Flow} = Q_{max} = 5.0 \times 10^{-3}\ m^3/s$$

A Schedule 40, nominal 3.0 inch stainless steel pipe was chosen for use as the particle collection cylinder (I.D. = 77.93 mm, Area = $4.77 \times 10^{-3}\ m^2$). The superficial velocity in the cylinder is:

$$\text{Velocity} = V_g = Q_{max}/\text{Area}$$
$$= 1.05\ m/s$$

Since the velocity is approximately 1 m/s, the SS pipe was considered to be suitable, and it was assumed that no reentrainment of particles would occur.

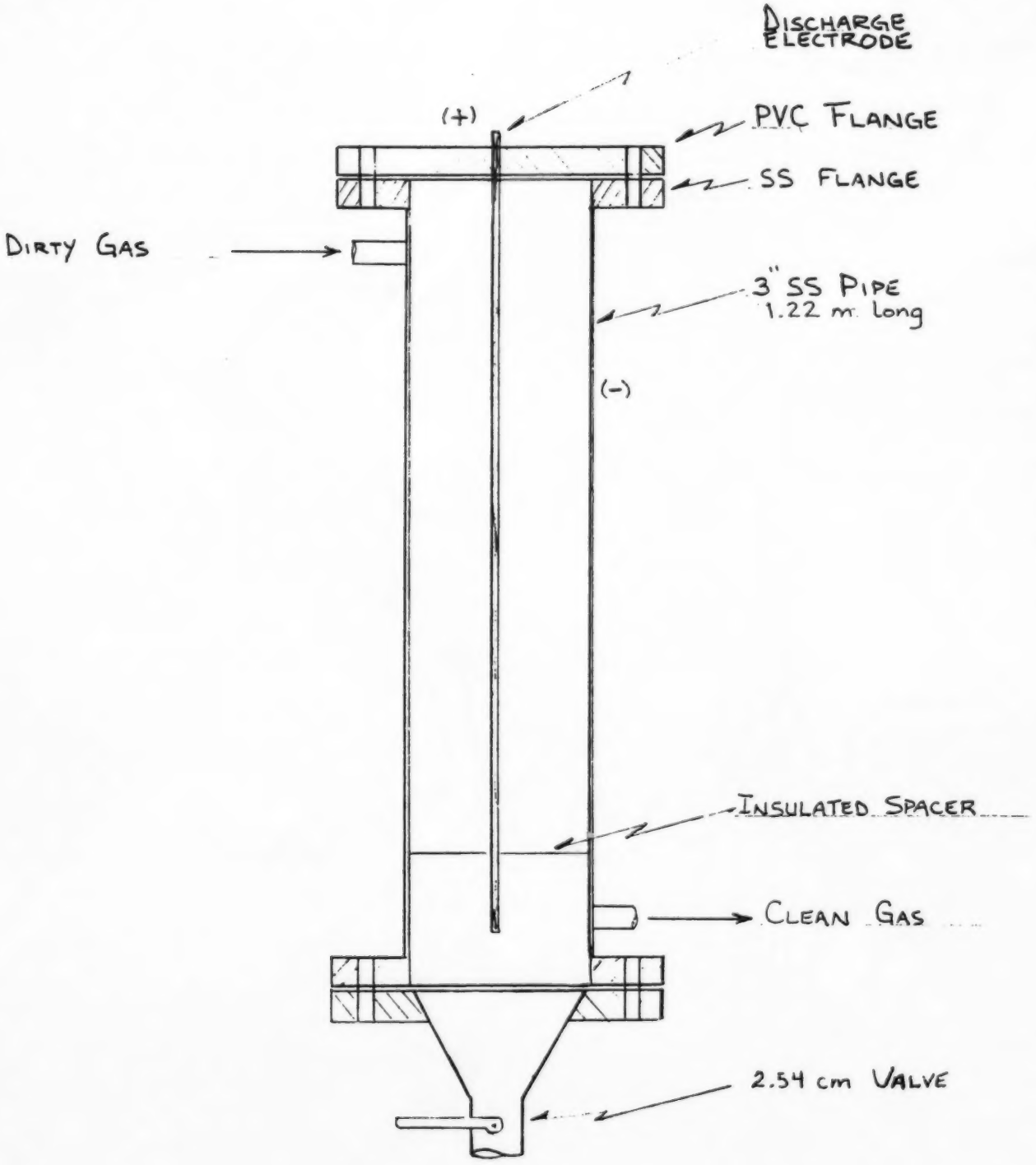


Figure 10.1. Rapid Thermal Processing of Gas Oil: Electorstatic Precipitator

The length of pipe chosen was 1.22 m. yielding a vapour residence time of 1.2 s. In order for the electrostatic precipitator to be effective there must be enough time for the smallest particles (typically the most difficult to remove) to be captured on the collection pipe. For a particle size of less than 2 microns (estimated for pyrolytic vapours) the migration velocity is 0.0335 m/s (0.11 ft/s) [3].

The migration distance (D_g) can then be found:

$$D_g = t * V_g$$
$$= 1.2 * 0.0335$$
$$= 0.04 \text{ m}$$

Since the collection pipe is 77.93 mm in diameter, a particle would have to migrated a distance of 38.97 mm to be captured on the wall of the collection cylinder. Because the migration distance D_g is greater than the actual distance that the particle must travel (i.e. 38.97 mm), under the "worst case" scenario all of the particles will be collected.

1. Blump, R.L. "Electrostatic Precipitators in Industry". Chemical Engineering. January 17 (1977).

2. Lewandowski, G.A. "Specifying Mechanical Design of Electrostatic Precipitators". Chemical Engineering. June 19 (1978).

3. Porter, H.F. "Gas Solid Systems". Chemical Engineers Handbook 5th Edition. McGraw-Hill. (1978).

10.2 Determination of the Moisture, and Loss on Ignition of the Catalyst Heat Carrier

10.2 Determination of the Moisture, and Loss on Ignition of the Catalyst Heat Carrier

To determine the amount of loss on ignition in each gas oil experiment the solid heat carrier from the catch pot and recovery equipment is ashed using American Society for Testing Materials (ASTM) procedures. A correction is made for the inherent ash content of the solid heat carrier. In the case of the sand heat carrier analysis yielded an average high temperature loss on ignition of 0.033 wt%. Analysis of the catalyst from Grace Davidson Co., reported only the total loss on ignition (7.8 wt%). This includes the moisture content as well as the high temperature loss on ignition. Since the moisture has been driven off, and out of the catalyst prior to an experiment, only the high temperature loss on ignition needs to be known for the purpose of correcting the product solid residue determination.

Since catalyst is very porous not only does water adhere (adsorbed) to the surface of the catalyst, but is also absorbed in the pores of the catalyst. The water which is trapped in the matrix of the catalyst is known as hydrated water. Hydrated water is much more difficult to drive out of the catalyst. Temperatures in excess of 450 C are necessary. For this reason the adsorbed, absorbed moisture content, and ash determination had to be determined in three steps:

1) A known amount of fresh catalyst was weighed and placed in a convection oven at 105 C.

2) The weighed sample from the convection oven was placed in a muffle furnace at 500 C under an inert atmosphere.

3) Following the determination of the hydrated water content the muffle furnace temperature was raised to 875 C and the catalyst combusted to determine the high temperature loss on ignition.

The following table illustrates the results of the analysis of five catalyst samples.

moisture content (in convection oven at 101 C)

TRIAL	CRUCIBLE (g)	(before) CATALYST & CRUCIBLE (g)	CATALYST (g)	(after) CATALYST & CRUCIBLE (g)	CATALYST (at 101 C) (g)	MOISTURE CONTENT (g)	MOISTURE CONTENT (%)
1	21.1412	52.1034	30.9622	52.0849	30.9437	0.0185	0.05975
2	22.3870	54.5240	32.1370	54.5237	32.1367	0.0003	0.00093
3	23.8629	53.8869	30.0240	53.8920	30.0291	0.00051	0.01699
4	22.6292	52.0046	29.3754	51.9955	29.3663	0.00091	0.03098
5	23.7163	52.7110	28.9947	52.6943	28.9780	0.0167	0.05760

hydrated water content (in muffle furnace at 500 C, N_2 atmosphere)

TRIAL	(after) CATALYST & CRUCIBLE (g)	CATALYST (g)	HYDRATED WATER (g)	HYDRATED WATER (%)
1	49.7030	28.5618	2.3819	7.693
2	52.0438	29.6568	2.4799	7.717
3	51.5792	27.7163	2.3128	7.703
4	49.7329	27.1037	2.2626	7.702
5	50.4691	26.7528	2.2252	7.674

high temperature loss on ignition (in muffle furnace at 875 C)

TRIAL	CATALYST & CRUCIBLE (g)	CATALYST (g)	HIGH TEMPERATURE LOI (g)	(%)
1	49.6111	28.4699	0.0919	0.323
2	51.9475	29.5605	0.0963	0.326
3	51.4013	27.5384	0.1779	0.646
4	49.6610	27.0318	0.0719	0.265
5	50.4184	26.7021	0.0507	0.191

10.3 Sample Data Sheets and Computer Printouts for a Selected Pyrolysis Experiment

Included are:

General Data Sheets
Orifice Meter Summary Sheet
Gas Product Summary
Mass Balance Data Sheet

525 °C
400 ms

RAPID THERMAL PROCESSING (RTP)

DATA SHEET

Run: C80-5 Date: June 13/88 Operators: BAF, D.C., J.H.

1) System Set Temperatures (Degrees C)

	Heat Carrier Furnaces			Reactor Furnaces	
	A	B	C		
Top Zone	650 C	650 C	____ C	Zone 1	550 C
Bottom Zone	650 C	650 C	____ C	Zone 2	550 C
				Zone 3	____ C

	MI Cables		
	A	B	C
Setting	650	650	____

2) System Temperatures (Degress C)

Room Temperature: 29 C

Time (min)	____	.5	3	5	7	____	____	____	____	
Thermocouple										Average
1) Heat Carrier Feeder 'A'										
2) Heat Carrier Feeder 'B'										
3) Heat Carrier Feeder 'C'										
4) Transport Line Inlet 'A'										
5) Transport Line Inlet 'B'										
6) Mellen Heater 'C'										
7) Feedstock Inlet Temperature	254	228	224	221						
8) Rapid Thermal Mixer	240	245	235	219						
9) Reactor Zone '1' (wall)	529	526	528	533						
10) Reactor Zone '2' (inside)	524	527	528	533						
11) Reactor Zone '2' (wall)										
12) Transport Line Inlet 'C'										
Mellen Heater 'B'	678	720	721	722						
14) Solids Separator Gas Exit	325	339	343	355						
15) Condenser Exit	323	40.4	91.4	93.2						
16) Secondary Condenser Exit	99	15.5	19.1	21						

Run: C60-2

Rotameters

Time (min) 2 4 6 8

Rotameter	read	psig	read	psig	read	psig	read	psig	read	psig	read	psig	read	psig	read	psig	read	psig	Average
Heat Carrier																			
Trans 'A'	33	18	33	18	33	18	33	18											
Fluid 'A'	21	19	21	19	21	19	20	19											
Trans 'B'	35	16	35	17	35	17.2	35	17.5											
Fluid 'B'	20	3.3	20	4	19	4	18	4											
Trans 'C'	102	5.5	102	6	102	6	102	6.5											
Fluid 'C'																			
Quench																			
Quench																			
Feedstock	57	52	57	53	57	54	57	54											

Pressures

Barometric Pressure: 30.14 in Hg

Feedstock Feeder Pressure: 0.3 0.3 ____ ____ psig Condenser: ____ ____ psig

Solids Catch Pot: 0.2 0.2 ____ ____ psig Filter: ____ ____ psig

Feedstock Flowrate

for solid feedstock ----) Motor Control Setting: ____ % → 4 turns
Cal. flowrate: 80 g/min

for solid or liquid feedstock

Weight of feed in hopper: 4250 g

Amount left at completion: 3610 g

Weight of feedstock fed: 640 g

Time of Pyrolysis: 9 min

Feedstock flowrate: 71 g/min

Run: CGO-2

5) Exit Orifice

Time (min)	0.5	1.5	2.0	3.0	4.0	5.0	6.5	7.0	8.0	Average
P_u :	27.6	28.4	28.1	27.8	28.3	28.4	28.7	28.6	28.5	29.0 cm H_2O
D_p :	13.1	13.5	13.4	13.3	13.7	13.6	13.8	13.8	13.7	13.9 cm H_2O

1308.8 g total feed

7) Sand Feeders

Estimated flow per feeder: _____ g/min

Total weight of sand fed: 18.0 kg

Time sand was fed: 11 min

Flowrate : 1636 g/min

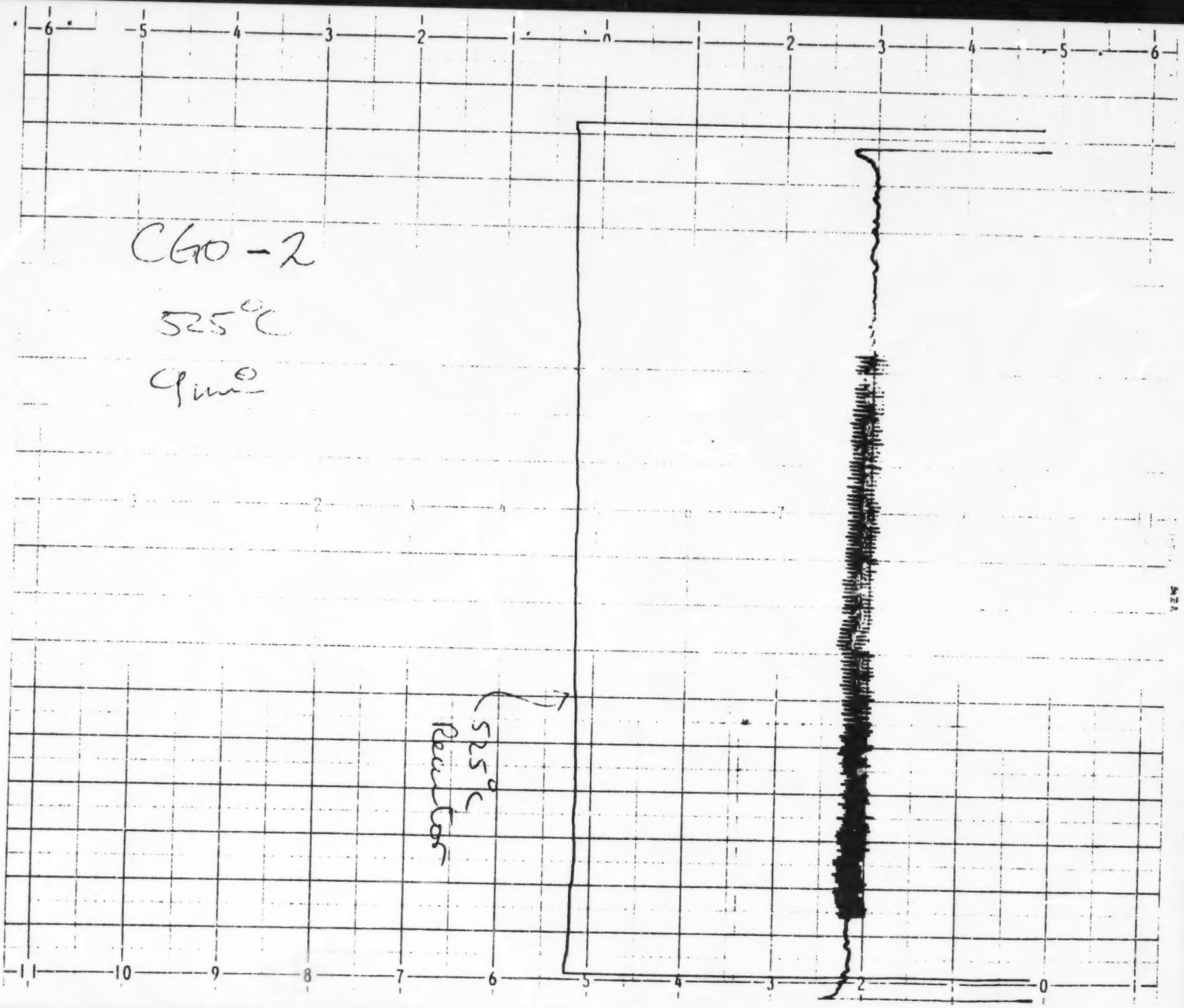
8) Collection Gag

Tank Pressure Before: 37.8 cm Hg
After Evacuation: 0.3 cm Hg

Difference: 37.5 cm Hg

Tank Temperature: 30 C

9) Comments


CG10-2
525°C
4 min
525°C
Reaction

PRODUCT SUMMARY Run: CGO-2 Date: 15-Jun-88 Reactor Temperature = 525 °C

Table 1. G.C. Calibration

Component	Calibration Area Values Sample 1	Sample 2	Sample 3	Average	Calibration Conc.	Average Resp. Factor
Hydrogen	55480	56008	0	55744	6.25	8919.0
Carbon Dioxide	110897	110253	0	110575	2.3	48076.1
Ethylene	59015	58721	0	58868	1.157	50879.9
Ethane	29703	29572	0	29637.5	0.548	54083.0
Acetylene	19973	26736	0	23354.5	0.518	45085.9
Oxygen	19598	20200	0	19899	0.528	37687.5
Nitrogen	2923912	2930998	0	2927455	76.39	38322.5
Methane	75630	77335	0	76482.5	2.172	35212.9
Carbon Monoxide	335238	336116	0	335677	8.425	39843.0
Benzene/Toluene	3413	3428	0	3420.5	0.04111	83203.6
Propane	33589	32965	0	33277	0.528	63024.6
Propylene	32480	32143	0	32311.5	0.528	61196.0
Hydrogen Sulfide	12110	15225	0	13667.5	0.49	27892.9
Propadiene	28096	27666	0	27881	0.5	55762.0
Butene-1	37404	37005	0	37204.5	0.518	71823.4
Isobutylene	42664	42219	0	42441.5	0.55	77166.4
Trans-Butene-2	39649	40436	0	40042.5	0.52	77004.8
Cis-Butene-2	36585	36019	0	36302	0.48	75629.2
Butadiene	216164	215907	0	216035.5	3.12	69242.1

Table 2. Bag G.C. Values

Component	Sample 1	Sample 2	Average
Hydrogen	0	0	0
Carbon Dioxide	1616	1590	1603
Ethylene	1466	1450	1458
Ethane	607	531	569
Acetylene	0	0	0
Oxygen	8153	7875	8014
Nitrogen	3786112	3789915	3789013.5
Methane	929	913	921
Carbon Monoxide	0	0	0
Benzene/Toluene	3899	3989	3944
Propane	0	0	0
Propylene	1098	1079	1088.5
Hydrogen Sulfide	0	0	0
Propadiene	0	0	0
Butene-1	0	0	0
Isobutylene	0	0	0
Trans-Butene-2	0	0	0
Cis-Butene-2	0	0	0
Butadiene	0	0	0

Table 3. G.C. Composition Summary (molar %)

Component	Molar Composition	Air Free Molar Comp.	Normal Molar Composition Air Free	Normal Molar Composition Nitrogen/Oxygen Free
Hydrogen	0.000	0.000	0.000	0.000
Carbon Dioxide	0.033	0.033	0.034	20.348
Ethylene	0.029	0.029	0.029	17.488
Ethane	0.011	0.011	0.011	6.420
Acetylene	0.000	0.000	0.000	0.000
Oxygen	0.213	0.000	0.000	0.000
Nitrogen	98.872	98.072	99.833	0.000
Methane	0.026	0.026	0.027	15.962
Carbon Monoxide	0.000	0.000	0.000	0.000
Benzene/Toluene	0.047	0.047	0.048	28.928
Propane	0.000	0.000	0.000	0.000
Propylene	0.018	0.018	0.018	10.855
Hydrogen Sulfide	0.000	0.000	0.000	0.000
Propadiene	0.000	0.000	0.000	0.000
Butene-1	0.000	0.000	0.000	0.000
Isobutylene	0.000	0.000	0.000	0.000
Trans-Butene-2	0.000	0.000	0.000	0.000
Cis-Butene-2	0.000	0.000	0.000	0.000
Butadiene	0.000	0.000	0.000	0.000
	99.25	98.24	100.00	100.00

Table 4. Summary of Product Gas Composition

Component	Mol. Wt.	Molecular Weight Contribution Air Free	Molecular Weight Contribution Nitrogen/Oxygen Free	Mass Fraction	Mass of Product Gas	Gas Yield (wt. %)
Hydrogen	2.02	0.000	0.000	0.00000	0.000	0.000
Carbon Dioxide	44.01	0.015	8.955	0.18835	0.769	0.120
Ethylene	28.05	0.008	4.905	0.10317	0.421	0.066
Ethane	30.07	0.003	1.931	0.04061	0.166	0.026
Acetylene	26.04	0.000	0.000	0.00000	0.000	0.000
Oxygen	32.00	0.000	0.000	0.00000	0.000	0.000
Nitrogen	28.02	27.973	0.000	0.00000	0.000	0.000
Methane	16.04	0.004	2.560	0.05385	0.220	0.034
Carbon Monoxide	28.01	0.000	0.000	0.00000	0.000	0.000
Benzene/Toluene	85.13	0.041	24.626	0.51795	2.114	0.330
Propane	44.09	0.000	0.000	0.00000	0.000	0.000
Propylene	42.08	0.008	4.568	0.09607	0.392	0.061
Hydrogen Sulfide	34.08	0.000	0.000	0.00000	0.000	0.000
Propadiene	40.07	0.000	0.000	0.00000	0.000	0.000
Butene-1	56.10	0.000	0.000	0.00000	0.000	0.000
Isobutylene	56.10	0.000	0.000	0.00000	0.000	0.000
Trans-Butene-2	56.10	0.000	0.000	0.00000	0.000	0.000
Cis-Butene-2	56.10	0.000	0.000	0.00000	0.000	0.000
Butadiene	54.10	0.000	0.000	0.00000	0.000	0.000
Total Process Gas Mol. Wt.	28.05			1.00	4.08	0.64
Product Gas Mol. Wt	47.55					

Table 5. Mass of Gas in the Bag and Orifice Meter

	Bag	Orifice	Total
Tank DP (cm Hg)	37.50		
Tank Temperature °C	30		
No. Moles (AF)	4.81		
Mass (gms AF)	134.94	1308.86	1443.80
No. Moles (N/O F)	0.008		
Product Gas (g)	0.38	3.70	4.08

Table 6. Mass Balance

Component	Mass (g)	
Feedstock	640	
Gas	4.08	0.64 %
Residue	10.17	1.59 %
Liquids	625.75	97.77 %

Mass Balance (products/feedstock) = 100.00 %

RTP Residence Time
****

Temperatures:	Feedstock	225 °C	
	Reactor	525 °C	
	Heat Carrier	650 °C	
	Quench	340 °C	
	Ambient	29 °C	
Pressures:	Ambient	30.14	1.01 Atm
	Reac. Inlt.	0.3	1.02 Atm
	Reac. outlt.	0.2	1.01 Atm

Rotameters:

Rotameter Designation	Reading	Pressure (psig)	Standard Mass Flow (g/min)	Actual Mass Flow (g/min)
Transport A	33	18	15.272	21.615
Fluid A	20	19	5.319	7.642
Transport B	35	17	16.410	22.870
Fluid B	20	4	5.319	5.700
Transport C	0	0	0.000	0.000
Fluid C	0	0	0.000	0.000
Quench 1	102	6.5	54.562	62.233
Quench 2	0	0	0.000	0.000
Feedstock	57	54	28.938	59.316

Total Nitrogen Carrier Gas Mass Flow Through The System = 179.375

Total Nitrogen Carrier Gas Mass Flow Through The Reactor = 117.142

Time of Pyrolysis: 9 min
Solid Heat Carrier 1636 g/min

Nitrogen Mass Balance Summary:

Total Nitrogen Through the System (rotameter calibration): 1614.38 g

System Summary
****

Feedstock:

Feedstock Flowrate:	71.11 g/min	----- Total =	640.00 g
Feedstock Trans. Gas Flowrate:	59.32 g/min	----- Total =	533.84 g
Solids Loading:	1.199 mass of feedstock/mass of trans. gas		

Heat Carrier:

Heat Carrier Flowrate:	1636.00 g/min	----- Total =	14724.00 g
Transport Gas Flowrate:	57.83 g/min	----- Total =	520.43 g
Solids Loading:	28.29 mass of sand/mass of trans. gas		

Reactor:

Solids to solids loading:	23.01 mass of sand/mass of feedstock
Total Mass of N2 Through the Reactor(orifice meter):	883.70 g
Total Mass of N2 Through the Reactor(rotameters):	1054.28 g
Density of Oil Vapour Through the Reactor:	2.485 g/l
Density of Carrier Gas Through the Reactor:	0.435 g/l
Volume Flow of Product Vapour:	0.429 l/s
Volume Flow of Carrier Gas (orifice meter):	3.761 l/s
Volume Flow of Carrier Gas (rotameters):	4.487 l/s
Volume of Reactor at 525 °C:	1.857 l
Residence Time (orifice meter determination):	443.21 ms
Residence Time (rotameter determination):	377.76 ms

10.4 Summary of the Results from the Analysis by Canmet of the Liquid and Solid Residue Product

Test #	Solids (Solvent) Used	Solids (wt%)						Liquid (wt%)				
		Catch Pot			Recovered from Process			As Received			Solvent-free	
		Moisture	Loss On Ignition	Carbon	Moisture	Loss On Ignition	Carbon	IBP-Solvent BP	IBP-216°C	IBP-343°C	Gasoline	Gasoline + Light Cycle Oil
Catalyst (DA-440) fresh		2.37	6.78	<0.02								
Catalyst (DA-440) Heated		3.72	2.83	<0.02								
Liq. Feed (SF135)								0.0	0.0	25.0	0.0	25.0
CGO-1	Sand (THF)	<0.02	<0.02	0.04	0.09	<0.02	0.13	2.0	5.0	31.5	3.1	30.1
CGO-2	Sand (THF)	0.02	<0.02	0.02	0.07	0.06	0.33	0.0	2.0	25.0	2.0	25.0
CGO-3	Sand (THF)	0.02	0.03	0.02	0.02	0.18	0.17	0.0	5.1	34.5	5.1	34.5
CGO-4	Sand (THF)	<0.02	<0.02	<0.02	0.06	0.13	0.44	0.0	8.8	40.0	8.8	40.0
CGO-5	Sand (Acetone)	0.02	<0.02	0.02	0.09	0.14	0.33	4.0	16.8	42.8	13.3	40.4
CGO-6	Catalyst (Acetone)	2.66	2.28	0.78	3.69	6.50	6.24	17.0	22.0	42.3	6.0	30.5
CGO-7 (pure Liq)	Sand (None)							0.0	9.0	45.0	9.0	45.0
CGO-7	Sand (Acetone)	0.02	<0.02	0.03	0.67*	1.74*	1.10*	45.0	50.6	69.0	10.2	43.6
CGO-8	Catalyst (Acetone)	0.10	0.04	0.10	0.38	11.89	9.96	8.0	20.4	55.5	13.5	51.6
CGO-9	Catalyst (Acetone)	<0.02	0.57	0.22	2.82	3.62	3.37	6.0	19.7	55.0	14.6	52.1

Solids recovered did not look like sand but catalyst

10.5 Summary of the Determination of the Light Cycle Oil, Decant Oil, Gasoline Yield, and Conversion

10.5 Summary of the Determination of the Light Cycle Oil, Decant Oil, Gasoline Yield, and Conversion

From the analysis carrier out at the Canmet laboratory, Appendix 10.4, a determination of the light cycle oil (LCO), Decant oil (DO), gasoline yield and product conversion was made. Since the yields given by Canmet were based on the liquid product and not on the percent of gas oil fed a conversion had to be made. By multiplying the normalized liquid yield by the percent of product in the liquid as determined by Canmet, the yield as a function of the gas oil fed was determined. A summary of the determination is given below.

Rapid Thermal Processing of Gas Oil: Gasoline, Decant Oil and Conversion Determination

Run	Normalized Liquid Yield	Light Cycle Oil	Decant Oil	Light Cycle Oil	Decant Oil	LCO + DO	Conversion	Gasoline	C_5/C_6	C_5/C_6 + Gasoline
	% of the feed	% of the liquid		% of the feedstock			(%)	% of the feedstock		
CGO-1	94.7	27.0	69.9	25.57	66.20	91.76	8.24	2.94	1.54	4.48
CGO-2	98.1	23.0	75.0	22.56	73.58	96.14	3.86	1.96	0.33	2.29
CGO-3	83.1	29.4	65.5	24.43	54.43	78.86	21.14	4.24	4.00	8.24
CGO-4	46.4	31.2	60.0	14.48	27.84	42.32	57.68	4.08	7.36	11.44
CGO-5	40.3	27.1	59.6	10.92	24.02	34.94	65.06	5.36	9.71	15.07
CGO-6	67.8	24.5	69.5	16.61	47.12	62.23	36.27	4.07	12.17	16.24
CGO-7	76.2	36.0	55.0	27.43	41.91	69.34	30.66	7.77	0.86	8.63
CGO-8	52.3	38.1	48.4	19.93	25.31	45.24	54.76	7.06	5.07	12.13
CGO-9	68.9	37.5	47.9	25.84	33.00	58.84	41.16	10.06	0.98	11.04

10.6 Summary of the Determination of the Maltenes, Asphaltenes, Carbenes and Carboids for the Gas Oil Pyrolysis Study

10.6 Summary of the Determination of the Maltenes, Asphaltenes, Carbenes and Carboids for the Gas Oil Pyrolysis Study

A sample of the liquid product was divided into standard fractions using the Soxhlet procedure outlined in Chapter 6. A summary of the maltene, asphaltene, and carbene/carboid determination is given below.

Sample	Thimble (g)	Mass of Thimble & Product (g)	Product (g)	After Pentane (g)	Maltene (g)	Maltene (%)	After Toluene (g)	Asphaltene (g)	Asphaltene (%)	Carbene/ Carboids (g)	Carbene/ Carboids (%)
CGO-1	50.8432	60.7986	9.9554	56.0018	4.7968	48.18	54.8764	1.1254	11.30	4.0332	40.51
CGO-1	33.1428	46.1709	13.0281	38.5121	7.6588	58.79	37.5524	0.9597	7.37	4.4096	33.85
CGO-2	30.4071	43.9876	13.5805	38.0888	5.8988	43.44	36.7762	1.3126	9.67	6.3691	46.90
CGO-2	50.999	64.0513	13.0523	56.4888	7.5625	57.94	55.9836	0.5052	3.87	4.9846	38.19
CGO-3	50.8784	61.3725	10.4941	56.1276	5.2449	49.98	54.9884	1.1392	10.86	4.11	39.16
CGO-3	3.122	46.0745	12.9525	39.4502	6.6243	51.14	36.8573	2.5929	20.02	3.7353	28.84
CGO-4	32.9591	47.6739	14.7148	46.4269	1.247	8.47	43.7609	2.726	18.53	10.7418	73.00
CGO-4	33.1269	39.9751	6.8482	39.3331	0.642	9.37	38.3773	0.9558	13.96	5.2504	76.67
CGO-5	35.0342	36.6398	1.6056	36.5827	0.0571	3.56	36.3699	0.2128	13.25	1.3357	83.19
CGO-6	34.7704	42.2054	7.435	38.0443	4.1611	55.97	36.6904	1.3539	18.21	1.92	25.82
CGO-6	49.2108	58.7012	9.4904	53.5417	5.1595	54.37	53.1014	0.4403	4.64	3.8906	41.00
CGO-7	51.8663	62.6621	10.7958	61.2352	1.4269	13.22	53.2369	7.9956	74.06	1.3733	12.72
CGO-7	34.971	48.6602	13.6892	44.2356	1.9353	14.85	39.9123	4.3233	33.18	6.7695	51.96
CGO-8	50.8674	62.2476	11.3802	61.1525	1.0951	9.62	56.5624	4.5901	40.33	5.695	50.04
CGO-8	30.4142	41.0263	10.6121	40.4911	0.5352	5.04	35.0612	5.4299	51.17	4.647	43.79
CGO-9	33.0379	45.4756	12.4377	43.2473	2.2283	17.92	39.0382	4.2091	33.84	6.0003	48.24